Isomerizing-Hydroboration of the Monounsaturated Fatty Acid Ester Methyl Oleate†

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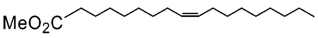
Biodiesel fuel, a mixture of fatty acid methyl esters (FAMEs) derived from plant oils, is increasingly available as a chemical feedstock. Methyl oleate (18:1), the 18-carbon monounsaturated FAME, is shown to undergo $[Ir(COE)_2Cl]_2$/dppe-catalyzed hydroboration with pinacolborane to give the product (**7**) in which the boronate ester group is in the terminal (C18) position. The formation of this product shows that the catalyst promotes both (1) the isomerization of the double bond from the 9,10-position of 18:1 to the terminal position and (2) the selective hydroboration of this isomer to give the product (**7**) in 45% yield. This tandem reaction should be capable of converting all isomers of 18:1 into the same product **7**.

Introduction

Biodiesel fuel is produced by the transesterification of various plant oils (e.g., soybean, corn, rapeseed/canola, and sunflower) with methanol. The resulting mixture of fatty acid methyl esters (FAMEs) consists of the esters of the fatty acids that were present as the triglycerides in the plant oils. The large-scale, economical production of biodiesel[1] makes it a potential feedstock for the manufacture of other chemicals.[2] Of particular importance for the studies described in this paper are oleic acid methyl ester (18:1)

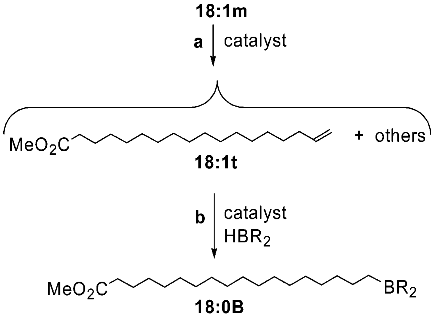


oleic acid methyl ester, 18:1

and the isomeric mixtures of monounsaturated fatty acids that are produced by partial hydrogenation of the polyunsaturated fatty acid esters present in plant oils. This hydrogenation can give FAME mixtures that consist of 90% monounsaturated FAMEs,[3,4] which could be used in the conversions described in this paper.

The strategy for the conversion of this monounsaturated FAME mixture (**18:1m**) into one product is outlined in Scheme 1. Step a involves a catalyst that rapidly isomerizes the double bond in each **18:1m** molecule to create a rapidly interconverting pool of **18:1m** isomers. From this pool of 33 possible positional and *cis*/*trans* isomers, we seek to react only the terminal isomer **18:1t**. Since this is the thermodynamically least-stable isomer (undetectable in our studies of the isomerization of methyl oleate), **18:1t** must be far more reactive in step b than all of the other isomers, which contain internal double bonds. As the **18:1t** isomer is depleted by the reaction in step b, it is replenished by the other **18:1m** isomers with which **18:1t** is in rapid equilibrium. In principle, the catalysts for steps a and b could be the same or two separate catalysts. There is evidence that both steps are catalyzed by one compound in the hydroboration of internal olefins. Thus, the hydroboration of *cis*-2-methyl-3-hexene with pinacolborane using Zr or Rh complex catalysts gives a product in which the boronate group is on the terminal carbon[5] Also, the reaction of 4-octene with pinacolborane, when catalyzed by $[Ir(COD)Cl]_2$ with dppe, where COD = 1,5-cyclooctadiene and dppe = bis(diphenylphosphino)ethane, gives a 78% yield of the terminal-boronated product.[6]

Scheme 1



Thus, the strategy outlined in Scheme 1 is viable using the internal alkenes described above, but it is not clear that it will be successful with the much longer hydrocarbon chains in **18:1m**. To our knowledge, the only report[7] of a successful tandem reaction involving rapid isomerization followed by a reaction selective for **18:1t** is that of the hydroformylation of 18:1 using a $Rh(acac)(CO)_2$ catalyst, where acac = acetylacetonate, together with a difficult-to-prepare diphosphite ligand. The reaction gave a 26% yield of the product, in which the aldehyde group was on the terminal carbon (C18). Although this reaction demonstrates the principle of tandem isomerization−hydroformylation

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† This paper is dedicated to Professor Jiabi Chen, Shanghai Institute of Organic Chemistry, on the occasion of his retirement and 65th birthday with thanks for his many contributions to organometallic chemistry.

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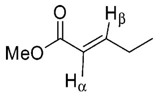
of methyl oleate (18:1), the yield was much lower than that (~88% yield) from analogous reactions of shorter chain alkenes that did not have an ester functionality such as 4-octene.[8,9]

In the present study, we initially explored olefin isomerization catalysts in order to determine the most favorable catalyst for promoting the rapid isomerization of 18:1 (step a). These studies were based on the previously reported olefin isomerization activity of the $[Ir(COE)_2Cl]_2/AgO_2CCF_3$ catalyst system, where COE = cyclooctene.[10] We then applied the $[Ir(COD)Cl]_2$/dppe catalyst, where dppe = $Ph_2PCH_2CH_2PPh_2$,[6] to the tandem isomerization−hydroboration of 18:1. This led to the most successful catalyst system $[Ir(COE)_2Cl]_2$/dppe for the conversion of 18:1 to the terminal boronated product (**18:0B**).

Experimental Section

All of the reactions were carried out under an argon atmosphere. Toluene, diethyl ether, methylene chloride, hexanes, and tetrahydrofuran were purified on alumina using a Solv-Tek solvent purification system, as described by Grubbs and co-workers.[11] $[Ir(COE)_2Cl]_2$[12] (COE = *cis*-cyclooctene) and $[Ir(COD)Cl]_2$[13] (COD = 1,5-cyclooctadiene) were synthesized by literature procedures. All other chemicals were reagent grade and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer (^1H at 400 MHz, ^{13}C at 100.6 MHz), while $^{11}B\{^1H\}$ spectra were recorded on an AC-200 spectrometer (^{11}B at 64.16 MHz). Internal references for the ^1H and ^{13}C chemical shifts are the deuterated solvents, while $^{11}B\{^1H\}$ shifts are reported relative to the external standard $F_3B{\cdot}OEt_2$. Mass spectra were recorded at 70 eV on a Finnigan Magnum ITD mass spectrometer.

Isomerization of Methyl *trans*-3-Pentenoate. To a solution of $[Ir(COE)_2Cl]_2$ (0.051 g, 0.057 mmol) in toluene (10 mL) were added methyl *trans*-3-pentenoate (0.18 mL, 1.5 mmol) and AgO_2CCF_3 (0.025 g, 0.11 mmol) successively under an argon flow. The resulting mixture was stirred for 1 h at 70 °C. The yellow color of the solution changed to purple within 5 min of stirring. The solution was filtered to remove AgCl, and the filtrate was evaporated. The crude product showed ^1H and ^{13}C NMR peaks corresponding to methyl *trans*-2-pentenoate (**2**) (65%) and other isomers (35%). The NMR peaks of **2** are nearly identical to those of an authentic sample of the compound. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.16 (m, 1H, H_β), 5.97 (d, $^3J_{HH}$ = 15.2 Hz, 1H, H_α), 3.84 (s, 3H, OMe), 1.83 (m, 2H, CH_2CH_3), 1.18 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 166.90 (C═O), 143.27 (C_β), 120.95 (C_α), 51.31 (OMe), 24.71 (CH_2), 11.60 (CH_3).



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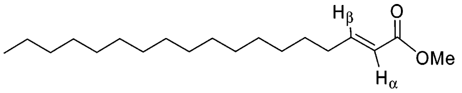
Isomerization of Methyl Oleate. To a solution of $[Ir(COE)_2Cl]_2$ (0.051 g, 0.057 mmol) in toluene (10 mL) were added methyl oleate (0.50 mL, 1.5 mmol) and AgO_2CCF_3 (0.025 g, 0.11 mmol) successively under an argon flow. The resulting mixture was stirred for 1 h at 70 °C. The yellow color of the solution changed to purple within 5 min of stirring. The solution was filtered to remove AgCl, and the filtrate was evaporated. The crude product showed distinctive ^1H NMR peaks corresponding to methyl octadec-*trans*-2-enoate (~4% of the mixture), which was described previously.[14] ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.91 (m, 1H, H_β), 5.81 (d, $^3J_{HH}$ = 15.2 Hz, 1H, H_α). In addition, a complex series of peaks for the other isomers were observed.



Hydroboration of Methyl 10-Undecenoate. A 10 mL round-bottom flask equipped with a magnetic stir bar and septum inlet was charged with $[Ir(COE)_2Cl]_2$ (0.030 g, 0.033 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (0.027 g, 0.066 mmol) under argon. Methylene chloride (3 mL) was added to give a clear orange solution, which was stirred for 5 min. To this solution were added methyl oleate (0.22 mL, 1.0 mmol) and pinacolborane (175 μL, 1.2 mmol); the reaction mixture was stirred for 12 h at room temperature. The resulting light yellow solution was diluted with 100 mL of methylene chloride and filtered through silica gel to remove the catalyst. The filtrate was then evaporated under reduced pressure to give a white solid, which was analyzed by ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy and GC/MS. Data for the (Bpin)−$(CH_2)_{10}$−CO_2Me (**5**) product (92% yield) are given below. The other major product as identified by GC/MS was methyl decanoate (**6**) (8%).

^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.59 (s, 3H, OMe), 2.23 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CO_2Me), 1.55 (m, 2H, CH_2CH_2−Bpin), 1.19 (s, 12H, Bpin), 1.18 (m, 14H, −CH_2−), 0.69 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2−Bpin). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 174.31 (C═O), 82.74 (Bpin), 51.38 (OMe), 34.07 (CH_2CO_2Me), 32.37 (CH_2CH_2−Bpin), 31.85 ($CH_2CH_2CO_2Me$), 29.51−29.12 (−CH_2−), 24.92 (Bpin), 24.74 (Bpin), 22.65 (CH_2−Bpin). $^{11}B\{^1H\}$ NMR (64.16 MHz, $CDCl_3$, 25 °C): δ 33.96. GC/MS (EI, 70 eV): *m/z* 326 [M^+], 294 [M^+ − OMe], 267 [M^+ − CO_2Me], 226 [(M^+ − $(CH_2)_3CO_2Me$], 194 [M^+ − $(CH_2)_5CO_2Me$], 170 [M^+ − $(CH_2)_3$Bpin], 167 [M^+ − $(CH_2)_7CO_2Me$], 126 [M^+ − $(CH_2)_{10}CO_2Me$].

Isomerizing Hydroboration of Methyl Oleate. A 10 mL round-bottom flask equipped with a magnetic stir bar and septum inlet was charged with $[Ir(COE)_2Cl]_2$ (0.030 g, 0.033 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (0.027 g, 0.066 mmol) under an argon flow. Methylene chloride (3 mL) was added to give a clear orange solution, which was stirred for 5 min. To this solution were added methyl oleate (0.34 mL, 1.0 mmol) and pinacolborane (175 μL, 1.2 mmol), and the reaction mixture was stirred for 24 h at room temperature. The resulting light yellow solution was diluted with 100 mL of methylene chloride and filtered through silica gel to remove the catalyst. The filtrate was then evaporated under reduced pressure to give a white solid, which was analyzed by ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy and GC/MS. Below are data for (Bpin)−$(CH_2)_{17}$−CO_2Me (**7**) (45% yield). The other major product was methyl stearate (47%), which was identified by GC/MS. Other unidentified products (8%) were also detected.

^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.65 (s, 3H, OMe), 2.28 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CO_2Me), 1.61 (m, 2H, CH_2CH_2−Bpin), 1.24 (m, 28H, −CH_2−), 1.23 (s, 12H, Bpin), 0.76 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2−Bpin). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 174.00 (C═O), 82.74 (Bpin), 51.11 (OMe), 33.81 (CH_2CO_2Me), 32.38 (CH_2CH_2−Bpin), 29.67−28.80 (−CH_2−), 24.92 (Bpin), 24.74 (Bpin), 22.65 (CH_2−Bpin). $^{11}B\{^1H\}$ NMR (64.16 MHz, $CDCl_3$, 25 °C): δ 30.01 ppm. GC/MS (EI, 70 eV): *m/z* 424 [M^+],

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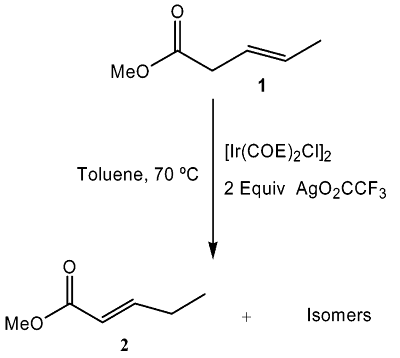
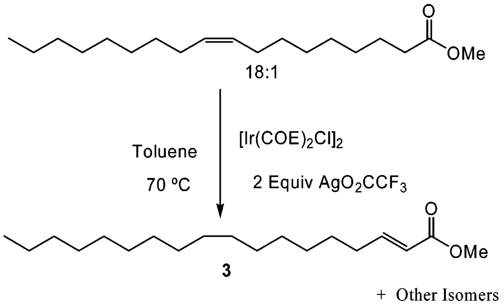
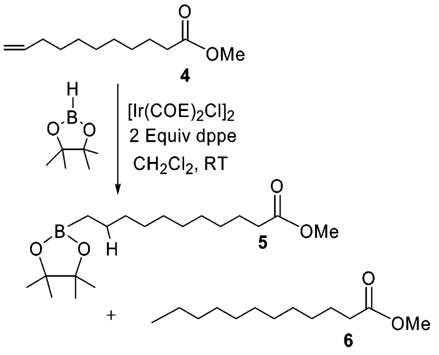
Scheme 2



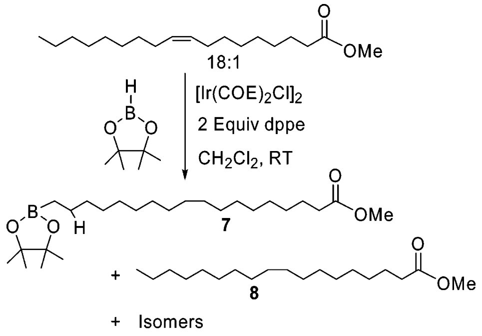
Scheme 3



Scheme 4



Scheme 5



324 [$M^+ - (CH_2)_3CO_2Me$], 264 [$M^+ - (CH_2)_4CO_2Me$], 255 [$M^+ - (CH_2)_3Bpin$], 198 [$M^+ - (CH_2)_{12}CO_2Me$], 142 [$M^+ - (CH_2)_{11}$-Bpin], 129 [$M^+ - (CH_2)_{12}Bpin$].

Results and Discussion

Isomerization of Methyl *trans*-3-Pentenoate. The isomerization of methyl *trans*-3-pentenoate was examined as a simple model for the more complicated isomerization of methyl oleate (18:1). When a toluene solution of methyl *trans*-3-pentenoate (**1**) (1.5 mmol) was heated at 70 °C in the presence of [$Ir(COE)_2Cl]_2$ (0.057 mmol) and AgO_2CCF_3 (0.11 mmol), the internal double bond in **1** isomerizes (Scheme 2) to give the α,β-unsaturated methyl ester **2** (65%) and other isomers (35%), which could include **1**. Product **2** was identified by peaks at 7.16 ppm (m) and 5.97 ppm ($^3J_{HH} = 15.2$ Hz), whose downfield positions are characteristic of the β and α olefinic protons of α,β-unsaturated esters;[14] the large coupling constant between them indicates that this is the *trans* alkene.

Isomerization of Methyl Oleate. The isomerization of methyl oleate (18:1) in a toluene solution containing [$Ir(COE)_2Cl]_2$ (0.057 mmol) and AgO_2CCF_3 (0.11 mmol) at 70 °C for 1 h gave an equilibrium mixture of different isomers (Scheme 3). The ^1H NMR spectrum of the mixture showed downfield signals at δ 6.91 ppm (m) and 5.81 ppm (d), indicating the presence of the α,β-unsaturated ester **3**; these peaks are very similar to those reported[14] earlier for **3**. The large coupling constant ($^3J_{HH} = 15.2$ Hz) between the α and β protons indicates that **3** is the *trans* isomer. The α,β-unsaturated ester **3** was obtained in ~4% yield as estimated from the ^1H NMR spectrum. This yield of **3** is essentially the same as that (3.5%) reported for the $RhCl(PPh_3)_3/SnCl_2$-catalyzed isomerization of 18:1.[14]

Hydroboration of Methyl 10-Undecenoate. Catalysis of the reaction of methyl 10-undecenoate (**4**) with pinacolborane (HBPin) (1.2 mmol) in methylene chloride by [$Ir(COE)_2Cl]_2$ (0.033 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (0.066 mmol) resulted in the formation of boronate ester **5** in 92% yield, along with the hydrogenation product **6** in 8% yield (Scheme 4). The formation of **5** was confirmed by ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy and GC/MS analysis. The ^1H NMR spectrum of the product mixture showed an upfield triplet at δ 0.69 ppm corresponding to the CH_2Bpin protons of **5**. In the $^{13}C\{^1H\}$NMR spectrum, the signal for CH_2-Bpin occurs at 22.64 ppm. These chemical shifts are similar to those reported for terminally functionalized boron products obtained from the hydroboration of 1-octene and 4-octenes.[5]

The mass spectrum of **5** showed a distinct molecular ion at *m/z* 326 and other peaks that are similar to those of methyl 10-undecenoate. Thus, the hydroboration of methyl 10-undecenoate (**4**) occurs regioselectively at the C11 atom, giving only the terminal boronate ester product (**5**). Recently, Yamamoto et al.[6] and Pereira and Srebnik[5] independently reported that pinacolborane hydroborates a wide variety of alkenes in the presence of iridium(I) and rhodium(I) catalysts, respectively. The major product in all cases was observed to be the terminal boronate isomer, even when an internal alkene was employed. Regioselectivity for the formation of the terminal boron products was attributed to the large steric requirements of pinacolborane. As for other boronate esters,[15] **5** should be easily converted to the corresponding alcohol.

Isomerizing-Hydroboration of Methyl Oleate. The reaction of methyl oleate (18:1) (1.0 mmol) with pinacolborane (1.2 mmol) is catalyzed by [$Ir(COE)_2Cl]_2$ (0.033 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (0.066 mmol) in methylene chloride at room temperature for 24 h to give boronate ester **7** (45%), along with the hydrogenation product methyl stearate (**8**) (47%) and some other unidentified isomers (8%) (Scheme 5). The identity of the boronate ester **7** was established by ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy and GC/MS analysis. In the ^1H NMR spectrum of the product mixture containing **7**, an upfield triplet at 0.76 ppm may be assigned to the CH_2Bpin

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protons. In the $^{13}C\{^1H\}$ spectrum of **7**, a resonance due to the carbon attached to the boron in the CH_2Bpin group occurs at 22.65 ppm. These chemical shifts are similar to those reported for terminally functionalized boron products formed in the hydroboration of 1-octene and 4-octenes.[6] Overlapping ^{13}C signals for the $-CH_2-$ carbons in the fatty acid ester chain are assigned to the peaks ranging from 28.80 to 29.67 ppm. The absence of products in which the Bpin group is on an internal carbon is indicated by the lack of complex ^1H and ^{13}C NMR signals expected for $CH_3-CH(Bpin)CH_2$ or $CH_2-CH(Bpin)-CH_2$ groups.

GC analysis of the product mixture showed three peaks at retention times of 12.0, 17.0, and 19.0 min. The peak at 12.0 min was assigned to the hydrogenation product, methyl stearate (**8**), by comparison to the retention time of a solution of commercial methyl stearate. In the GC/MS, the peak at 17.0 min showed a *m*/*z* value of 424, which corresponds to the molecular ion $[M^+]$ of **7**. The remainder of the mass spectrum of **7** exhibited a fragmentation pattern similar to that of methyl stearate (**8**). The peak at 19.0 min, although it clearly is a boron-containing product on the basis of its mass spectrum, was not identified. Quantitative GC analysis of the mixture using a known amount of methyl heptadecanoate (17:0) as an internal standard showed that >98% of the original methyl oleate (18:1) was converted to the products, which consisted of the terminal boronate ester **7** (45%), **8** (47%), and smaller amounts of unidentified compounds.

The above results show that the C=C double bond in methyl oleate (18:1) isomerizes in the presence of the catalyst $[Ir(COE)_2Cl]_2$/dppe and that the terminal olefin isomer selectively undergoes hydroboration to give the terminal boronate ester **7**. However, unlike the $[Ir(COD)Cl]_2$/dppe-catalyzed hydroboration of 4-octenes, which gave no hydrogenation products,[6] the hydroboration of methyl oleate resulted in the formation of a significant amount of methyl stearate (**8**). Perhaps, this indicates that the rate of isomerization of methyl oleate (**3**) is slower than that of 4-octene because hydrogenation products are observed in hydroboration reactions of sterically demanding (slow reacting) alkenes, as investigated by Burgess et al. using Wilkinson's catalyst.[16] Also, Behr et al. attributed the formation of a significant amount of hydrogenation product (**8**) in the isomerizing-hydroformylation of methyl oleate to a slower rate of isomerization for 18:1.[7] It is also possible that hydroboration of the α,β-unsaturated ester isomer **3** leads to the hydrogenation product **8**. Early studies by Brown and Keblys[17] showed that the α,β-unsaturated ester ethyl acrylate undergoes considerable hydrogenation to give ethyl propionate with either diborane or disiamylborane along with the hydroboration product. The authors proposed a mechanism involving an intermediate in which the borane hydrogen adds to the β carbon and the boron adds to the ester carbonyl oxygen. Hydrolysis of this intermediate gives the ethyl propionate product. Since this reaction occurs even at 0 °C, it is possible that isomer **3** reacts rapidly with pinacolborane to give the observed methyl stearate product **8**. The water required for this reaction would presumably come from the air when the reaction mixture is exposed to air prior to the GC analysis.

To understand the role of the $[Ir(COE)_2Cl]_2$/dppe catalyst, the reaction of 18:1 with pinacolborane was attempted without the catalyst under the usual conditions (Scheme 5); however, there was no reaction. It is conceivable that the role of the catalyst is to catalyze only the hydroboration of 18:1 to give a product in which boron is on either the 9 or 10 carbon atom. The resulting boronate ester might then isomerize (uncatalyzed) to give the terminal boronate ester product **7**; such isomerizations to give products with the boron on the terminal position are known to occur in other systems[18] often at higher temperatures than those used in the present studies. In the present system, it seems unlikely that such an isomerization occurs because it is known[19] that the tris(carbomethoxyalkyl)borane (with the boron on the 9 or 10 position), formed in the reaction of methyl oleate (18:1) with diborane, undergoes little or no isomerization in refluxing diglyme (bp 162 °C) during 24 h. Thus, the evidence suggests that the $[Ir(COE)_2Cl]_2$/dppe-catalyzed reaction of 18:1 and pinacolborane to give **7** (Scheme 5) occurs by an $[Ir(COE)Cl]_2$/dppe-catalyzed isomerization of 18:1 followed by an $[Ir(COE)Cl]_2$/dppe-catalyzed hydroboration of the terminal isomer **18:1t**, as described in Scheme 1.

In an attempt to improve the yield of the desired terminally boron-functionalized methyl ester (**7**) and to reduce the amount of methyl stearate (**8**), the reaction was conducted at 0 °C. However, at this lower temperature, the yield of **7** decreased while that of **8** increased. At 0 °C, the yield of **7** was 26% and that of **8** was 61%; this compares with 45% and 47% for **7** and **8**, respectively, when the reaction was conducted at room temperature. The lower yield at 0 °C could be attributed to the slower rate of isomerization of methyl oleate at the lower temperature.

To determine the effect of the phosphine on the product distribution, dppm, $Ph_2PCH_2PPh_2$, was used instead of dppe. Under the same conditions used with dppe, the reaction of 18:1 (1.0 mmol) and pinacolborane (1.2 mmol) in the presence of $[Ir(COE)_2Cl]_2$ (0.033 mmol) and dppm (0.066 mmol) in CH_2Cl_2 at room temperature for 24 h gave a slightly lower yield of **7** (40%), as well as **8** (50%) and 10% of unreacted 18:1. When PPh_3 (0.132 mmol) was used as the phosphine cocatalyst under the same conditions, only 15% **7** was observed together with 40% **8** and 45% unreacted 18:1. Thus, dppe is the most effective phosphine cocatalyst.

We also evaluated the catalytic activity of $[Ir(COD)Cl]_2$ for the hydroboration of methyl oleate with pinacolborane under similar reaction conditions. Thus, the reaction of 18:1 (1.0 mmol) with pinacolborane (1.20 mmol) in CH_2Cl_2 was conducted in the presence of $[Ir(COD)Cl]_2$ (0.033 mmol) and dppe (0.066 mmol) at room temperature for 24 h. However, no formation of **7** was observed. On the other hand, when the reaction was performed at 50 °C for 24 h, **7** (25% yield) and **8** (40% yield) were produced, but a substantial amount of unreacted methyl oleate (35%) also remained.

The influence of different solvents on the isomerizing-hydroboration of methyl oleate was also examined. As shown in Table 1, the solvent seems to have only a small influence on the yield of the terminal boronate ester (**7**). However, methylene chloride is the solvent of choice because it gives a slightly higher yield of **7** and complete consumption of the methyl oleate (Table 1).

Conclusions

The goal of this project was to explore the possibility that methyl oleate (18:1) would undergo selective hydroboration to give a product in which the boronate ester group is exclusively

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Table 1. Solvent Effects on the Product Distribution of the $[Ir(COE)Cl]_2$/dppe-Catalyzed Hydroboration of Methyl Oleate (Scheme 4)[a]

	% yield of the different products[b]			
solvent	**3**	**8**	**9**	other isomers
CH_2Cl_2	0	45	47	8
benzene	6	43	43	8
benzene	9	41	46	4

[a] Reaction conditions: methyl oleate (18:1) (1.0 mmol), pinacolborane (1.20 mmol), $[Ir(COE)_2Cl]_2$ (0.033 mmol), dppe (0.066 mmol), room temperature, 24 h. [b] % yield was determined by GC analysis.

on the terminal carbon. The observed 45% yield of this product (Scheme 5) shows that the $[Ir(COE)_2Cl]_2$/dppe catalyst is capable of promoting both the rapid isomerization of methyl oleate and the selective hydroboration of the terminal isomer **18:1t**. The success of these studies indicates that other isomers of **18:1m**, obtainable by partial hydrogenation of FAMEs from various plant oils, can be similarly transformed into the boronate ester **7**. Moreover, these results suggest that the mixture of monounsaturated FAMEs (**18:1m**) can be used as a feedstock for the preparation of other terminally functionalized derivatives of methyl stearate.

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Supporting Information Available: ^1H, ^{13}C NMR and mass spectra of **5** and **7**. This material is available free of charge at http://pubs.acs.org.

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